Oxygenation and Oxidation of Manganese(II) Complexes of *NN*-Ethylenebis(salicylideneimine) and Analogues

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Summary From the reaction of Mn^{II}(salen) or Mn^{II}(3-methoxy-salen),H_2O with oxygen in organic solvents, three types of complexes have been isolated, which contain $Mn^{III}–O_2–Mn^{III}$, $[Mn^{IV}–O]_n$, or $Mn^{IV}=O$ bonds.

IT is known that Co^{II}(salen), [salen = *NN*-ethylenebis(salicylideneiminato) dianion], combines reversibly with molecular oxygen either in solution or in solid state,[1-3] and Fe^{II}(salen) gives a μ-oxo-complex $[Fe^{II}(salen)]_2O$ by reaction with oxygen in solution.[4] Recently, Lewis *et al.*[5] have reported that in *NN*-dimethylformamide (dmf) or pyridine (py) solution, Mn^{II}(salen) is readily oxidized by air to form an insoluble brown product, for which they suggested a polymeric structure with binuclear $[Mn(salen)]_2$-O,H_2O as a unit.

We report that three types of complexes have been obtained when Mn^{II}(salen) or Mn^{II}(3-methoxy-salen),H_2O reacts with oxygen in organic solvents. The complexes contain, respectively, $Mn^{III}–O_2–Mn^{III}$, $[Mn^{IV}–O]_n$, and $Mn^{IV}=O$ bonds: the type of complex obtained depends on the solvent used and on the substituent.

$[Mn^{III}(salen)]_2O_2$: A solution of Mn^{II}(salen) in dimethyl sulphoxide was kept in an oxygen atmosphere at room temperature for *ca.* 24 h. Reddish-brown crystals were precipitated, together with a brown amorphous compound. The crystalline product is slightly soluble in Me_2SO, $HCONMe_2$, and CH_2Cl_2, and it could be extracted with a large volume of CH_2Cl_2. By evaporating the solvent, a fine crystalline complex was obtained. The elemental analysis agrees with the formula Mn(salen)O. The t.g.a. curve of the complex shows a weight loss near 200° which corresponds to the elimination of 0·5 mole of O_2 per Mn atom, and does not show any subsequent weight loss up to 350°. On heating *in vacuo* near 200° for 1 h, the complex was converted into the Mn^{II}(salen) in 85% yield. The combined oxygen could not be removed by passing N_2 through the dimethylformamide solution. Thus, on the basis of the analysis and other evidence, the complex is formulated as a μ-peroxo-complex $[Mn^{III}(salen)]_2O_2$. The magnetic susceptibility measurement for a solid sample at 296·5K gives μ_{eff} = 2·79 B.M., which corresponds to two unpaired electrons. As for Mn^{III}(salen)X, magnetic moments are reported to be 4·96 B.M. for X = Br and 4·98 B.M. for X = 1, indicating four unpaired electrons.[6] Thus it is considered that in the μ-peroxo-complex spin-pairing is caused in the central Mn^{III} by bonding with $(O_2)^{2-}$ ion.

$[Mn^{IV}(salen)O]_n$: On reaction of Mn^{II}(salen) with oxygen in dmf or py solution, a brown, amorphous compound was precipitated. This is insoluble in all common solvents, and the analysis corresponds to the formula Mn(salen)O. The magnetic moment of 1·97 B.M. obtained for the complex is very close to that reported for Lewis' complex.[5] The t.g.a. curve shows a weight loss near 200°. Although this appears to be due to the elimination of O, this is obscured by a subsequent decomposition. From the properties, the complex may be regarded as a polymeric catena-oxo-complex, $[Mn(salen)O]_n$. The complex shows an i.r. spectrum identical with that of the insoluble amorphous compound described above.

$[Mn^{IV}(3\text{-methoxy-salen})O]_n$: $Mn^{II}(3\text{-methoxy-salen}),H_2O$ forms an insoluble, brown complex with oxygen in either Me_2SO, py, or dmf. The analysis agrees with the formula given.

$O{=}Mn^{IV}(3\text{-methoxy-salen}),1{\cdot}5CH_3OH$: A methanol solution of $Mn^{II}(3\text{-methoxy-salen}),H_2O$ was kept in an oxygen atmosphere for 12 h. Evaporation of the solution gave dark green needles. The analysis agrees with the formula $MnO(3\text{-methoxy-salen}),1{\cdot}5CH_3OH$. In the t.g.a. curve, the elimination of 1·5 moles of CH_3OH per Mn was observed between 70 and 140°, and a decomposition occurred at a lower temperature (*ca.* 150°) than in the case of the other complexes. The magnetic moment is 3·68 B.M., indicating a high-spin state of Mn^{IV}. The complex can be converted quantitatively into the insoluble $[Mn(3\text{-methoxy-salen})O]_n$ by dissolving it in dmf, py, or Me_2SO. The oxo-manganese(IV) complex may be considered an intermediate in the formation of the catena-oxo-manganese(IV) complex.

The results of manometric experiments on oxygen absorption at 20° are consistent with the formulae of the complexes.

TABLE

Complex	Solvent	O_2/Mn
Mn^{II}(salen)	Me_2SO	0·53
Mn^{II}(salen)	dmf	0·46
Mn^{II}(3-methoxy-salen), H_2O ..	Me_2SO	0·47

The present results suggest that there would be a difference between the reaction rates in forming μ-peroxo-manganese(III) and oxo-manganese(IV) complexes. The rates depend on the solvent used and the substituent on the Schiff base.

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